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COMPARING CARBONATE AND ORGANIC AMS-¹⁴C AGES IN LAKE ABIYATA SEDIMENTS (ETHIOPIA): HYDROCHEMISTRY AND PALEOENVIRONMENTAL IMPLICATIONS

Elisabeth Gibert¹ • Yves Travi² • Marc Massault¹ • Tesfaye Chernet² • Florent Barbecot¹ • Fatima Laggoun-Defarge³

ABSTRACT. We studied a 12.6-m-long sequence from Lake Abiyata (Central Ethiopia) to establish a reliable and accurate chronology for use in global paleoclimatic reconstructions. The 26 accelerator mass spectrometry radiocarbon (AMS ¹⁴C) ages, performed on carbonates and organic matter, define 2 parallel chronologies, representing the complete Holocene period. However, these chronologies show a significant discrepancy from 500 to 900 BP in depth; ages obtained on carbonates were always older than those on organic matter. The hydrogeological and geochemical behavior of the Lake Abiyata basin has shed light on this discrepancy. We found that the carbonate crystallization is due mainly to the mixing of lake waters with groundwaters from the multi-layered aquifer contained in the 600-m-thick basement of the lake. The ¹⁴C activity of total dissolved inorganic carbon (TDIC) measured by AMS from bottom and surface lake waters (111.4 and 111.8 pMC, respectively) confirms that the mixing occurs at the water-sediment interface. This evidence of groundwater participation in the carbonate crystallization calls into question the current paleoclimatic reconstructions based on inorganic carbonates in lakes. Specific attention should thus be given to the respective proportions of each end-member in the mixing for the quantitative estimation of the groundwater input. This will help to validate the paleoenvironmental reconstructions and to highlight an eventual diagenetical evolution of inorganic carbonates during burial, via the study of pore waters.

INTRODUCTION

For several decades, efforts have concentrated on the multidisciplinary study of climatic archives in the tropics because they represent key regions in the present-day monsoonal circulation, as well as its reconstruction during the Quaternary. Despite specific and complex meteorological features such as air masses stopped eastward by the Rift Valley and the Turkana Jet, which enhances aridity (Nicholson 1996), it has been shown that long-term rainfall variations in eastern Africa are linked to quasi-global climate fluctuations, with major changes in atmospheric circulation and/or moisture balance since the Last Glacial Maximum at 18,000 BP (uncalibrated time scale; Webb et al. 1993; Rozanski et al. 1996).

Lacustrine cored sequences are some of the most useful materials for continental paleoclimate studies because they often present sensitive, continuous records of past environments with high sedimentary rates. Despite the fact that studies previously conducted on the Ziway-Shala basin (Lakes region, central Ethiopia) have focused on outcropping sections along the Bulbula River (Figure 1; Gasse and Street 1978; Street 1981; Bonnefille et al. 1986), several lacustrine transgressive/regressive phases have been registered in the basin during the Late Pleistocene-Holocene period. The first one is the Ziway-Shala IV (Z-S IV), occurring at 11,500 BP. After 10,000 BP, evidence was found for 3 major lake highstands: 1) Z-S V from 9950 to 8500 BP; 2) Z-S VI between 6500 and 4800 BP; and 3) Z-S VII, starting shortly after 2500 BP.

All these Late Pleistocene-Holocene highstands caused the 4 lakes to be connected, producing a large, unique lake (Street 1981; Figure 1). Therefore, the Ziway-Shala basin represents a unique, important basin that is highly sensitive to hydrological fluctuations, and so, is a key site for an accu-

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rate reconstruction of Late Quaternary paleoenvironmental changes in east Africa (Gasse and Street 1978; Street 1981; Gillespie et al. 1983; Bonnefille et al. 1986; Johnson 1996).

The main problem encountered for such paleoclimatic reconstructions remains the establishment of reliable ^{14}C time scales (e.g. PAGES Report 1995; Johnson 1996; Gasse et al. 1990; Talbot and Johannessen 1993; Fontes et al. 1992, 1993, 1996; Talbot and Kelts 1996; Colman et al. 1996), especially in sites subjected to intense volcano-tectonic activity (mainly along the Wonji Fault belt; Le Turdu et al. 1999; Figure 1), and for which lacustrine deposits may have registered climatic and tectonic events simultaneously during specific phases.

Solving this problem requires the calculation of the initial ^{14}C activity of water from which authigenic materials have been formed, with at least 2 essential goals:

1. To determine a reliable, accurate chronological framework of the cored lacustrine sequence based on authigenic samples. This also requires that there be no evidence of post-sedimentary geochemical evolution. Many processes can modify, partly or completely, the original isotopic signature of such materials: (i) the disequilibrium in ^{14}C activity between atmospheric CO_2 and the total dissolved inorganic carbon (TDIC) of surface water (so-called "reservoir effect"); (ii) ^{14}C -free CO_2 inputs either along faults, or geothermal springs (sometimes dominant process in tectonically active areas) or via large aquifers connected to the lake and where radioactive decay has occurred (the so-called "hard water effect" *sensu stricto*); (iii) percolation of humic compounds or chemical exchanges with pore water after deposition; (iv) mixing between authigenic and reworked materials; and (v) coring artifacts as well as contamination during core transportation and/or analytical treatments. The first 3 propositions are related to the origin of the TDIC in lake waters (Fontes and Gasse 1991; Fontes et al. 1996). Such evolutions may influence both authigenic carbonates and organic matter of aquatic origin, and in most cases, ^{14}C dates will only represent apparent ages (e.g. Durand et al. 1984; Fontes et al. 1996). Furthermore, as described in Geyh, Schotterer and Grosjean (1998), the month-to-month evolution of the TDIC within a year of inorganic carbonate crystallization and/or CO_2 consumption during organic matter development may also induce a *temporal* discrepancy in the ^{14}C datings of such materials in CaCO_3 -type lakes.
2. To both calibrate and ensure the validity of past environmental scenarios reconstructed via the stable isotope contents of authigenic materials such as the ^{13}C and ^{18}O contents of inorganic carbonates, or the ^{13}C and ^{15}N contents of organic matter (Gasse et al. 1991; Fontes et al. 1996; Talbot and Kelts 1996).

In this study, we present 26 AMS- ^{14}C dates which were obtained on a 12.5-m-long sedimentary sequence cored in Lake Abiyata in 1994 performed on either inorganic carbonates or organic matter. The comparison of the carbonate and organic dates allows us to better understand the discrepancy observed between these 2 series in relation to the hydrological and hydrochemical processes and background that exist in Lake Abiyata.

DESCRIPTIVE BACKGROUND

Lake Abiyata ($7^{\circ}40'\text{N}$, $38^{\circ}40'\text{E}$; 1500 m asl; Figure 1) is part of the Ziway-Shala basin, located in the 100-km-long tectonic closed structure related to the NNE–SSW caldera system. It is in the axial zone of the Main Ethiopian Rift. The Ziway-Shala basin is bordered to the east by the Arussi-Bale Massif and to the west by the Shewan plateau.

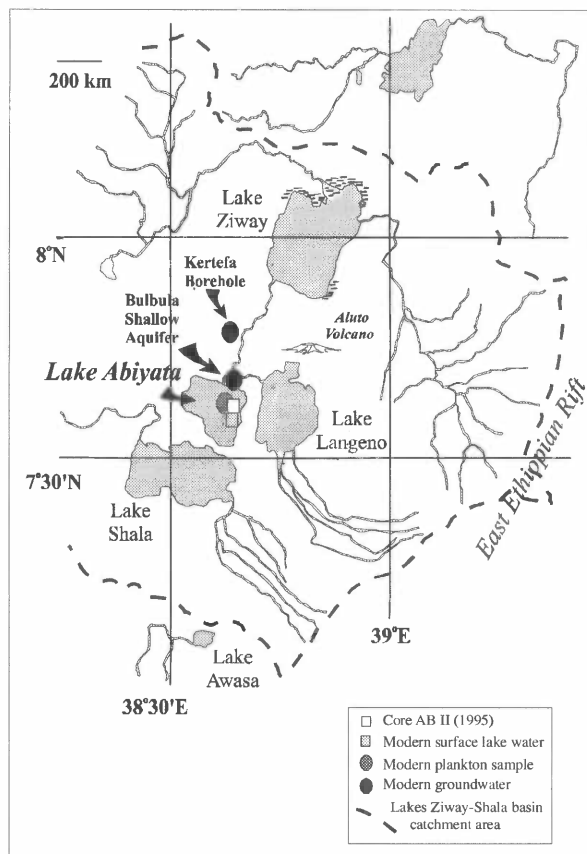


Figure 1 Lake Abiyata, East Ethiopian Rift

Lake Abiyata, which has been considered the final stage of sedimentary infilling of the basin, corresponds to a half, deep graben. Its catchment area is limited to the east by the NNE–SSW faults of the Katlo horst, and to the west by the volcanic systems linked to the Shala volcano. Its northern shore opens on the Bulbula alluvial plain where the thickness of lacustrine and alluvial deposits can reach 600 m (Le Turdu et al. 1999). The western and southwestern margins of Lake Abiyata have shown volcanic activities at 0.18 Ma. Since then, only very slight tectonic movements from the NNE fault system during the Holocene are suspected (Le Turdu et al. 1999), in agreement with the

eastward migration of tectonic activity of the East African Rift. Despite the fact that intense geothermal activity is observed at the Corbetti and Aluto volcanic centers (Le Turdu et al. 1999; Figure 1), geothermal springs do not influence the Lake Abiyata basin.

Modern Hydrological System

The region has a tropical–monsoonal climate, with a mean annual precipitation of 1180 mm and a mean annual temperature of 16.3 °C (Addis-Ababa station; Figure 1; IAEA/WMO Network; Rozanski et al. 1996). The pluviometric regime is driven by the yearly oscillation of the intertropical convergence zone (ITCZ), which determines a warm-wet summer (maximum rainfall from June to September) and a dry, cold and windy winter.

A simple surface network, mainly developed upstream (around Lake Ziway), connects the 3 northern lakes of the basin via the Horakelo River from Lake Ziway to Lake Abiyata, and the Bulbula River from Lake Ziway to Lake Langeno (Figure 1). Lake Abiyata is therefore the terminal lake of the Ziway-Langeno-Abiyata subsystem, since no present-day surface connection exists between Lake Abiyata and Lake Shala.

Although Lake Ziway receives the most important input of surface waters from the whole basin, chemically speaking, it remains a highly stable reservoir (Figure 1; Chernet 1998). The majority of this inflowing water returns to the atmosphere by evaporation, while only 10% comes out as evaporated surface flows towards Lake Abiyata.

The lacustrine sedimentary basement of the Lake Abiyata basin is characterized by a multi-layered aquifer in which 2 main levels are exploited: (1) the alluvial shallow aquifer of the Bulbula Plain connected to the lake and supporting most of the local village water-supply wells; and (2) a deeper system exploited by the Soda Ash Plant. Despite some clayey lens, which can cause the deeper aquifer to be locally confined, these 2 producing levels can be considered hydraulically connected at the basin scale. Groundwater flowpaths move towards Lake Shala, which has the lowest elevation (1550 m; Chernet 1998). In that context, modern surface water of Lake Abiyata is composed of a mixture of surface water (80%) and groundwaters of the Bulbula alluvial plain (20%; Travi et al. 1997; Chernet 1998).

Under modern evaporative conditions, lake waters evolve from an alkaline to a highly alkaline type chemical facies due to the disequilibrium between HCO_3^- and concentrations of earth-alkali elements. This is in agreement with what is known about terminal lakes in ignimbrite areas (Travi et al. 1997). In such catchments, calcite saturation is quickly reached, and the resulting calcite—or magnesium calcite—precipitation leads to a very low chemical activity of calcium. Lake Abiyata modern waters are sodi-carbonate-dominated. The waters are characterized by a temperature of 22.5 °C, an electric conductivity of 25.5 mS cm⁻¹, and a pH of 10.1 (at sampling time and coring site; Figure 1). Therefore, the hyper-alkalinization process, marked and enhanced by evaporation, affirms the small content in dissolved calcium of Lake Abiyata surface waters (Table 1; $\text{IS}_{\text{Lake Abiyata surface water}} = 0.215$; PC-Wateq-4 Programme: Ball and Nordstrom 1991; AQUA Programme: Valles and de Cockborne 1992). Calcite precipitation cannot take place in such a system without any other additional source of calcium which may arise from mixing with Ca-type waters.

MATERIALS

The 12.6-m piston-cored sequence studied was taken in 1995 from the southeastern part of Lake Abiyata (core ABII) as far as possible from detrital input from former rivers (Figure 1), and under a 7-m water depth. The core consists mainly of shell-free, homogeneous clayey and organic muds,

Table 1 Chemical contents of some surface water and groundwater—Lake Abiyata basin, Ethiopia. Sampling date November 1994. See Figure 1 for sample locations. The chemical analyses in bold type correspond to the ones used for the calculation of the respective mixing proportions (see Discussion).

Sample	pH	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	HCO ₃ ⁻ (mg L ⁻¹)	CO ₃ ²⁻ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	F ⁻ (mg L ⁻¹)
Lake Ziway	8.6	73	18	12.9	6.8	266	11	11.1	2.4	1.4
Lake Langano	9.2	361	34	4.6	6.5	649	72	151.0	11.2	14.0
Lake Abiyata	10.1	6019	519	0.35	1.9	7712	3500	2654.0	242.0	243.0
Meki River	8.5	35	5	19.8	40.3	204	6	6.6	12.5	0.6
Bulbula borehole	8.2	297	16	12.1	91.1	966	0	17.6	8.2	18.3
Neguele Arsi Borehole	7.5	29	4	14.5	2.9	198	0	2.6	1.5	0.8
Gonde spring (ignimbrite)	7.4	8	4	8.1	3.8	40	0	2.3	2.2	0.2
Soda Ash plant	9.1	1167	11	0.6	15.7	2008	30	481.0	189.9	51.5
Kertefa borehole	8.3	365	24	6.3	0.2	603	8	154.1	99.5	0.7

Table 2 Palynofacies observations and countings (%) of selected samples from core ABII

Depth (cm)	Planktonic AOM	Algae	Zooclasts	Slightly oxidized		Pyro- fusinite	Preserved brownish	Gelified debris	Mushroom mycelium tissues		Pyrite
				debris	debris						
46.0	77	2	2	15	0	0	0	4	0	0	0
228.5	84	1	0	11	0.5	0	0	1	0	0	2.5
339.5	63	0	1	31	1.5	0	0	2.5	1	0	0
450.4	50	1	0	42	5	1	1	1	0	0	0
744.5	56	2	0	31	9	1	1	1	0	0	0
1036.5	50.5	2	1	27.5	7	1	1	3	1	6	6

alternating with finely (260–270, 710–720 and 770–780 cm) or coarsely (320–380 cm) laminated sandy marls (Figure 2). The increase in the number of tephra layers downwards correlates to increasing numbers of coarse sandy layers.

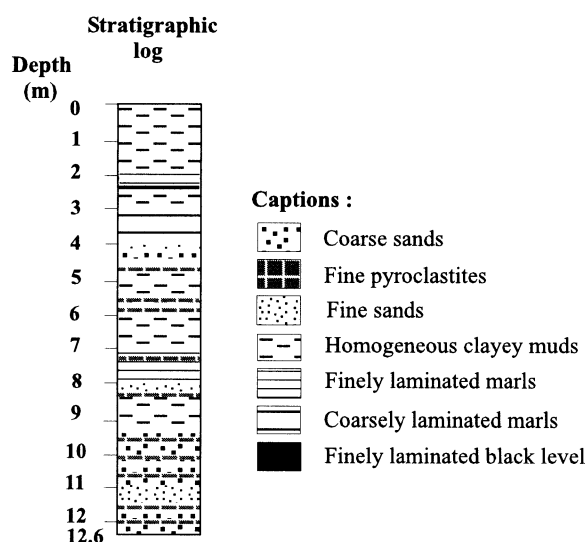


Figure 2 Core ABII, Lake Abiyata, Ethiopia (1995)

The modern sedimentation of Lake Abiyata is dominated by lacustrine organic matter due to an intense primary productivity. Its reduced catchment area and the lack of inflowing rivers preclude inputs of important detrital vegetation debris, and reduce the sedimentation of pedogenetic organic matter. These field observations have been confirmed by palynofacies analyses of organic compounds from 6 specific ^{14}C -dated levels⁴ (Table 2). These levels contain mainly phytoplanktonic organic matter, with a maximum of 84% at 228.5 cm depth. On the other hand, the most common well preserved ligno-cellulosic (LC) debris, either translucent or brownish, is almost absent from the samples (<1%), showing the lack of input from emergent plants or local vegetation growing around the lake.

Gelified debris result from organic remains having been submitted to a very fast evolution toward colloid formation in water. These debris have the same origin as oxidized fragments, and reveal 1) a short residence time in soils; 2) anoxic conditions at the lake bottom; and 3) no (or very low) diagenetical effects before sedimentation. Pyrofusinite particles result from allochthonous influx and can be windblown from a far distance. Although the particles are increasing downwards and are roughly associated with the increasing numbers of ash layers, they are absent from the top of the core, likely indicating no present-day aeolian inputs to the lake.

⁴For palynofacies observations, the total organic matter (TOM) is isolated from the mineral matrix by acidic attacks (HCl and HF acids), and mounted on slides as according the standard procedure. The OM was observed through transmitted light-microscopy for a characterization of the origin and preservation degree of the different organic components. In order to achieve countings of each organic fraction, samples were also submitted to a K-NaOH treatment to remove humic acids, and bromide-alcohol mixing for density separation.

RESULTS

Modern Samples

The selection of authigenic materials for ^{14}C dating has been based on microscopic observations of the deposits. Since no charcoal or macrophyte remains have been found, our selection has concentrated on total organic matter (TOM). Samples from sedimentary zones characterized by coarse deposits, either marls or sands, have been eliminated to the extent possible.

The ^{14}C activity of modern lake surface waters (^{14}C Act. = 111.6 percent modern carbon [pMC]; $\delta^{13}\text{C}_{\text{TDIC}} [\text{‰ vs. PDB}] = +3.5$; $\delta^{13}\text{C}_{\text{CO}_2 \text{ eq.}} [\text{‰ vs. PDB}] = -4.6$ with $T = 22^\circ\text{C}$) demonstrates the present-day equilibrium between the TDIC and the atmospheric reservoir (Levin et al. 1992, 1980). The slight difference between $\delta^{13}\text{C}_{\text{TDIC}}$ and $\delta^{13}\text{C}_{\text{CO}_2 \text{ eq.}}$ is likely due to the respective ^{13}C re-equilibration rates between the pairs *primary organic matter/dissolved ^{13}C* and *dissolved ^{13}C /atmospheric CO_2* . In addition to palynofacies observations, which have highlighted the very short residence time of organic input from the lake catchment area, phytoplanktonic organic matter at sampling time (mid-day algal bloom) develops in equilibrium with surface lake waters (^{14}C Act._{modern plankton} [pMC] = 111.4; $\delta^{13}\text{C}_{\text{modern plankton}} [\text{‰ vs. PDB}] = -21.5$), and represents an authigenic material. We have assumed that the ^{14}C activity of present-day primary production has been constant through time. Although they represent maximum ages due to the presence of pedogenetic organic debris, these calculated ^{14}C dates from bulk samples should be very close to the true ages (very small amounts of pedogenetic remains) and thus can be considered valid.

The ^{14}C chronology of the AB-II core is based on 13 datings performed on TOM, and completed on low organic content levels with 9 datings on inorganic carbonates⁵ (Table 3). Although both sets of data from both organic and carbonate components are in agreement with the stratigraphy, the 2 chronologies present a systematic and significant (although fluctuating) discrepancy. The time-lag is between 600 and 1500 yr, the ^{14}C ages defined on carbonates always being older than the ones on TOM (Tables 3 and 4; Figure 3).

We aim to examine this anomaly within the hydrological, hydrochemical, and sedimentological background of the Lake Abiyata basin. Such aging of the inorganic carbonates can only be explained through an input of ^{14}C -free/ ^{14}C -depleted carbon, either during precipitation or by diagenetical processes. In our case, and in contrast to what is proposed by Geyh et al. (1998) for most of the chronological interpretation of ^{14}C dates in lakes, this ^{14}C -free/ ^{14}C -depleted carbon input does not have to be considered constant through time. For a given level, the comparison between ^{14}C ages on TOM and ^{14}C ages on carbonates allows for the calculation of q , a coefficient that can be considered to reflect the proportion of ^{14}C -free/ ^{14}C -depleted carbon at that level (Table 3):

$$\text{For TOM:} \quad A = A_0 \cdot e^{-\lambda t} \quad (1)$$

with A and A_0 , the measured and initial ^{14}C activities of authigenic organic matter, respectively.

$$\text{For inorganic carbonates:} \quad A' = A'_0 \cdot e^{-\lambda t} \quad (2)$$

⁵The ^{14}C preparation for organic samples has consisted of a strong acid-alkali-acid (AAA) treatment, which was applied on both samples and reference blanks. For carbonated samples, the removal of the low organic content has been achieved through a weak H_2O_2 -leaching.

Table 3 Measured and calibrated ^{14}C datings of sediments from core ABII

Depth (cm)	Type ^a	Sample nr (Orsay)	^{14}C activity (pMC)	Measured ^{14}C age (yr BP)	Calibrated ^{14}C ages (cal yr BP) ^b	Ref. ^c	$\delta^{13}\text{C}$ TOM (‰ vs. PDB)	$\delta^{13}\text{C}$ CaCO_3 (‰ vs. PDB)
7.0	TOM	H-1945	101 ± 0.8	100 ± 60	40 (270/0 [present day])	(1)		
7.0	CaCO_3	H-1941	93.1 ± 0.7	580 ± 60				+2.21
46.0	TOM	H-1372	89.8 ± 0.6	865 ± 60	740 (890/700)	(1)	−19.31	
127.1	CaCO_3	H-1949	80.3 ± 0.6	1760 ± 60				+3.75
228.5	TOM	H-1415	80.0 ± 0.9	1790 ± 70	1710 (1810/1610)	(1)		
293.0	CaCO_3	H-1904	64.9 ± 0.6	3480 ± 70				+3.75
339.5	TOM	H-1365	68.0 ± 0.7	3100 ± 60	3310 (3370/3220)	(2)	−17.33	
450.4	TOM	H-1418	64.6 ± 1.0	3510 ± 80	3775 (3880/3650)	(2)	−19.23	
551.8	TOM	H-2010	61.3 ± 0.6	3900 ± 90	4345 (4425/4155)	(2)	−22.16	
551.8	CaCO_3	H-2007	51.1 ± 0.7	5400 ± 90				
671.5	TOM	H-2011	53.7 ± 0.6	4900 ± 100	5630 (5730/5500)	(1)	−23.75	
671.5	CaCO_3	H-2008	45.1 ± 1.5	6400 ± 100				
748.5	CaCO_3	H-1944	48.6 ± 0.5	5800 ± 80				+2.50
794.8	TOM	H-1480	51.5 ± 0.4	5330 ± 60	6140 (6195/5995)	(1)	−24.12	
794.8	CaCO_3	H-1906	47.3 ± 0.5	6010 ± 80				+2.80
824.6	CaCO_3	H-1902	43.6 ± 0.5	6660 ± 80				+2.80
838.5	TOM	H-1481	46.2 ± 0.3	6200 ± 60	7100 (7175/7010)	(1)	−25.11	
885.1	TOM	H-1419	41.3 ± 1.0	7100 ± 80	7910 (7940/7805)	(1)	−23.54	
939.0	TOM	H-1374	37.4 ± 0.4	7900 ± 90	8625 (8950/8550)	(3, 4)	—	
941.5	CaCO_3	H-2009	33.8 ± 0.9	8700 ± 90				+2.23
984.5	TOM	H-1483	33.3 ± 0.3	8830 ± 80	9870 (9920/9660)	(5)	−25.81	
984.5	CaCO_3	H-1903	29.4 ± 0.4	9830 ± 110				+2.00
1024.0	CaCO_3	H-1901	28.6 ± 0.4	10,050 ± 100				+2.00
1036.5	TOM	H-1417	31.8 ± 1.2	9200 ± 100	10,205 (10,300/10,035)	(5)	—	
1115.5	TOM	H-1416	28.6 ± 1.3	10,050 ± 100	11,350 (11,885/11,010)	(5, 6)	−23.19	
1253.5	CaCO_3	H-1893	21.7 ± 0.4	12,270 ± 130				+1.71

^aTOM: Total organic matter. CaCO_3 : calcite (and low magnesium calcite). Error bars represent one sigma deviation. Accuracies on ^{13}C measurements are of ±0.05 and ±0.02‰ PDB for carbonates and organic matter, respectively.

^bCALIB 3.0: Stuiver and Reimer (1993): 215–230.

^cReferences: Calibration 1993, *Radiocarbon* 35(1), 1993. (1) Stuiver M, Pearson GW, p 1–23; (2) Pearson GW, Stuiver M, p 25–33; (3) Pearson GW, Becker B, Qua F, p 93–104; (4) Linick TW, Long A, Damon PE, Ferguson CW, p 943–53; (5) Kromer B, Becker B, p 125–35; (6) Bard E, Arnold M, Fairbanks RG, Hamelin B, p 191–9; (4) Pearson GW, Stuiver M, p 25–33.

with A' and A'_0 , the measured and initial ^{14}C activities of of inorganic carbonates, respectively. The true ^{14}C age that would have to be found for inorganic carbonates is as follows:

$$A = A'_0 \cdot q \cdot e^{-\lambda t} = A_0 \cdot e^{-\lambda t} \quad (3)$$

with q , proportion of ^{14}C -free/ ^{14}C -depleted carbon at that level. Therefore,

$$1 = \frac{A_0 \cdot e^{-\lambda t}}{A'_0 \cdot q \cdot e^{-\lambda t}} = \frac{A_0}{A'_0 \cdot q} \quad (4)$$

$$q = \frac{A_0}{A'_0} \quad (5)$$

Consequently, q is constant for a given sample. Considering that A_0 , is equal to 100 pMC (^{14}C activity BP), the initial ^{14}C activity of water in which the inorganic carbonates have precipitated is thus equal to A_0/q , i.e. $100/q$ (Table 4).

Mixing Processes

Based on the 6 pairs of samples analyzed (Table 4), the interpolated curve highlights that the ^{14}C -free/ ^{14}C -depleted carbon input fluctuates along the core (Figure 3). These fluctuations are likely related to the lake level variations in both amplitudes and origin (tectonic and/or climatic). Several hypotheses can be put forward (Figure 4):

1. *Carbonate precipitation in surface waters, without any post-sedimentary evolution.* As presented above and despite strong evaporative conditions (mean $\delta^{18}\text{O}_{\text{modern lake surface waters [‰ vs. SMOW]}}=8.5$; $n=8$), the crystallization of inorganic calcite could not have occurred in Lake Abiyata modern surface water due to its very low calcium content. However, during the rainy season, flooding events could have supplied the lake water with enough calcium to induce the significant precipitation of carbonates (Travi et al. 1997). This water input would have reinforced the equilibrium between the surface water TDIC and the atmospheric CO_2 . This cannot account for the ^{14}C lag observed between fossil organic matter and carbonates. Superimposed on this eventual calcium input, the consumption of ^{13}C -depleted CO_2 by organic matter during photosynthesis (midday algal bloom occurring in the first 10 cm of the water column) would raise in the displacement of the calco-carbonic equilibria, and would also induce calcite precipitation. This process would have enhanced the precipitation of ^{13}C -enriched carbonates, the ^{13}C fractionation factor between the precipitated calcite and dissolved CO_2 being -10.4‰ at 25 °C . Although this seems to fit with the $\delta^{13}\text{C}$ values measured for inorganic carbonates (Table 3), the co-existing fractionation factor with respect to ^{14}C would have produced an aging of the initial ^{14}C activity of only 2 pMC (Saliège and Fontes 1983), lower than the 6.9 pMC observed for the core top (7-cm level).
2. *Early diagenetical processes at the water/sediment interface.* Although no chemical or isotopic data are available on the present-day interstitial water, CO_2 is generally released at the water/sediment interface during the very first steps of lacustrine organic matter oxidation. Following the calco-carbonic equilibria, and with no evidence of pH control by other chemical species, this increase in CO_2 concentration would immediately induce a decrease in pH, which would tend to inhibit early-diagenetical calcite precipitation. Finally, although complex dissolution/precipitation processes may occur at the surface of the newly crystallized calcite, the very low content of dissolved calcium and carbonated fraction cannot account for the observed ^{14}C discrepancies.
3. *Deep ^{14}C -free CO_2 rising along the main faults of the basin.* The ^{14}C activities of inorganic carbonates can be easily interpreted by considering the hypothesis of deep ^{14}C -free CO_2 rising along faults. On one hand, the modern chemical contents allow the calculation of the CO_2 partial pressure (pCO_2) of groundwater from the Kertefa borehole, i.e. $\sim 10^{-2.88}$ (Table 1; PC-Wateq-4 Programme; Ball and Nordstrom 1991). This calculated value is higher than that of the atmosphere ($\text{pCO}_2_{\text{atmosphere}} = 10^{-3.5}$), and does not demonstrate a deep CO_2 input in the aquifer. On the other hand, it seems very unlikely that deep CO_2 could have accounted for the post-sedimentary aging of fossil inorganic carbonates since the Lake Abiyata area constitutes the more stable part of the basin and does not present any active fault. However, the modern release of deep CO_2 observed in the deeper part of Lake Langeno (Figure 1), and greatly influencing its CITD all along the water column (EG, unpublished results), would not have modified that of Lake Abiyata even during highstands: 1) the geochemical influence of this deep CO_2 rapidly

decreases on both sides of the fault in Lake Langano; and 2) during highstands, the Lake surface/Lake deepness ratio increases, allowing for better equilibration of TDIC with atmospheric CO_2 .

4. *Mixing with groundwater.* The participation of old groundwater remains the only possible source of 1) enough dissolved calcium to allow for calcite precipitation; and 2) enough ^{14}C -free carbon via the calco-carbonic system to account for the older carbonate fraction. In such a case, calcite precipitation likely occurs through the mixing of lake water and groundwater at the water/sediment interface since the 1) low groundwater flow; 2) re-equilibration of groundwater with lake water, through degassing process (although very low); and 3) difference in temperature between the 2 end-members of the mixing allow for this calcite precipitation.

The following calculation can demonstrate that the hypothesis of mixing between lake water and groundwater is valuable, although such a hypothesis would require an exhaustive study of the chemical and physical evolution of groundwater in the basin. Previous and ongoing studies (Travi et al. 1997; Chernet 1998; Chernet et al. 1999) indicate that groundwater sampled in the Kertefa borehole drilled in the central part of the Bulbula plain can be considered representative of the aquifer under the lake and is taken as the groundwater end-member.

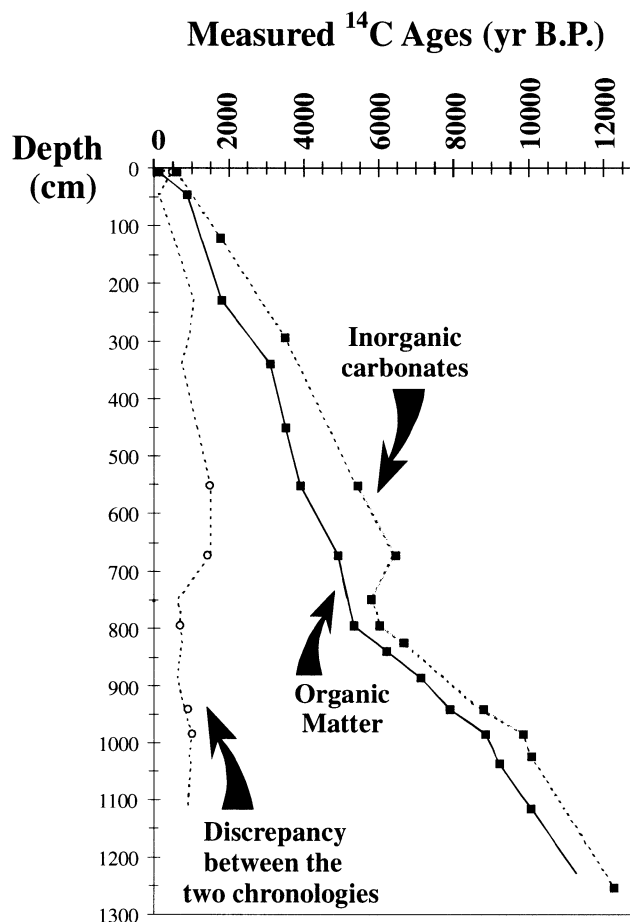


Figure 3 Radiocarbon chronology of core ABII-1995. Black and dashed curves correspond to datings on organic matter and inorganic carbonates, respectively. Empty circles represent the radiocarbon discrepancy for every pair of datings.

Table 4 Comparison of the discrepancy between ages on inorganic carbonates and organic matter at specific levels, and calculation of the dilution factor, q

Depth (cm)	¹⁴ C Age TOM (yr BP)	Measured activity of inorganic carbonates (pMC)	¹⁴ C Age CaCO ₃ (yr BP)	Δ (yr)	Initial activity of inorganic carbonates (pMC)	q
7.0	100 ± 60	93.1 ± 0.7	580 ± 60	480	94.3	1.061
551.8	3900 ± 90	51.1 ± 0.7	5400 ± 90	1500	83.0	1.204
671.5	4900 ± 100	45.1 ± 1.5	6400 ± 100	1500	83.0	1.205
794.8	5330 ± 60	47.3 ± 0.5	6010 ± 80	680	91.8	1.089
939.0/941.5	7900 ± 90	33.8 ± 0.9	8700 ± 90	800	90.4	1.107
984.5	8830 ± 80	29.4 ± 0.4	9830 ± 110	1000	88.2	1.133

Considering that the equilibrium between the TDIC of the lake surface water and the atmospheric CO₂ remained constant through time, the respective parts of lake water and groundwater in the mixing can be calculated as follows:

$$N_{\text{mixed water}} = X \cdot N_{\text{POLE I}} + (1 - X) \cdot N_{\text{POLE II}} \quad (6)$$

with $N_{\text{mixed water}}$, $N_{\text{POLE I}}$, $N_{\text{POLE II}}$, the number of ¹⁴C atoms in the mixed water, POLE I and POLE II, respectively; X, fraction of lake water in the mixing; 1-X, fraction of groundwater in the mixing.

On one hand, the measured ¹⁴C activity of a sample expressed in pMC can be converted in true activity as follows:

$$A = \frac{{}^{14}\text{C Activity}_{\text{measured}} \cdot 13.56}{100} \quad \text{in dpm} \cdot \text{g}^{-1}. \quad (7)$$

On the other hand, the true activity corresponds to

$$A = \lambda \cdot N$$

with λ , radioactive decay constant, in mn^{-1}
and N , number of ¹⁴C atoms.

From equations (6) and (7), we define the number of ¹⁴C atoms of a specific sample

$$N = \frac{1}{\lambda} \cdot \frac{{}^{14}\text{C Activity}_{\text{measured}} \cdot 13.56}{100} \quad \text{for 1 g of carbon.} \quad (8)$$

In order to describe the mixing between lake water and groundwater at the water sediment interface, we have to express the number of ¹⁴C atoms versus 1 L of water, knowing the total dissolved inorganic carbon content of the solution (TDIC = Total Carbon = TC, in $\text{mol} \cdot \text{L}^{-1}$)

$$N = \frac{1}{\lambda} \cdot \frac{{}^{14}\text{C Activity}_{\text{measured}} \cdot 13.56 \cdot (\text{TC} \cdot 12)}{100} \quad \text{for 1 L of water} \quad (9)$$

with λ , in mn^{-1}
and 12, molar weight of carbon.

In that case, every end-member can be defined as follows:

$$N_{\text{POLE I (Lake Abiyata)}} = \frac{\left(\frac{A_{\text{POLE I}}}{100}\right) \cdot 13.56 \cdot (TC_{\text{POLE I}} \cdot 12)}{\lambda} = \frac{(TC_{\text{POLE I}} \cdot 12) \cdot 13.56}{\lambda} \quad (10)$$

$$N_{\text{POLE II (groundwater)}} = \frac{\left(\frac{A_{\text{POLE II}}}{100}\right) \cdot 13.56 \cdot (TC_{\text{POLE II}} \cdot 12)}{\lambda} \quad (11)$$

with

$A_{\text{POLE I}}$, measured ^{14}C activity of POLE I,

$A_{\text{POLE II}}$, measured ^{14}C activity of POLE II,

λ , in mn^{-1} .

A simple mass balance model between the 2 end-members of the mixing, i.e. lake water and groundwater, allow first for the calculation of the respective ^{14}C atoms number and total carbon content resulting mixed water. As feedback in the calculations, it then allows for the establishment of the ^{14}C activity evolution curve with respect to the respective contributions of the 2 end-members (Figure 5; Table 5).

$$^{14}\text{C Activity}_{(\text{inorganic carbonates})} = \frac{100 \cdot N_{\text{mixed water}} \cdot \lambda}{13.56 \cdot (TC_{\text{mixed water}} \cdot 12)} \quad (12)$$

with $N_{\text{mixed water}}$, number of ^{14}C atoms per liter in the resulting water,

and $TC_{\text{mixed water}}$, Total Carbon Content (mol L^{-1}) in the resulting water.

The calculations have been realized entering the 2 extreme values of $[\text{HCO}_3^-]_{\text{Lake}}$ in the model, as deduced from the modern hydrological behavior of the basin, the modern geochemical evolution between Lakes Ziway and Abiyata having been considered to reflect the evolution of Lake Abiyata through time. These 2 values are 500 and 7000 mg L^{-1} , and represent respectively the present-day HCO_3^- concentration of Lake Ziway (*open* system end-member) and Lake Abiyata (*closed* system end-member). The buffered value of groundwater from the Kertefa borehole (groundwater end-member) has been chosen for the calculation.

Following the model, the transposition of these HCO_3^- concentrations in percentages of water volumes indicates mixing proportions compatible with the hydrological and hydrogeological *open* system, which seems to have prevailed during the Late and Middle Holocene (Table 5). Both water fluxes and total carbon concentration of the aquifer can be considered constant through time in the whole basin, and they define the basic level. Conversely, in Lake Abiyata, water inputs in the lake and the total carbon content of surface water evolve in opposite phases since a decrease in the HCO_3^- concentration corresponds to a high lake level. This would thus lead to an increase in the discrepancy between the 2 chronologies defined on carbonates and organic matter during lacustrine highstands.

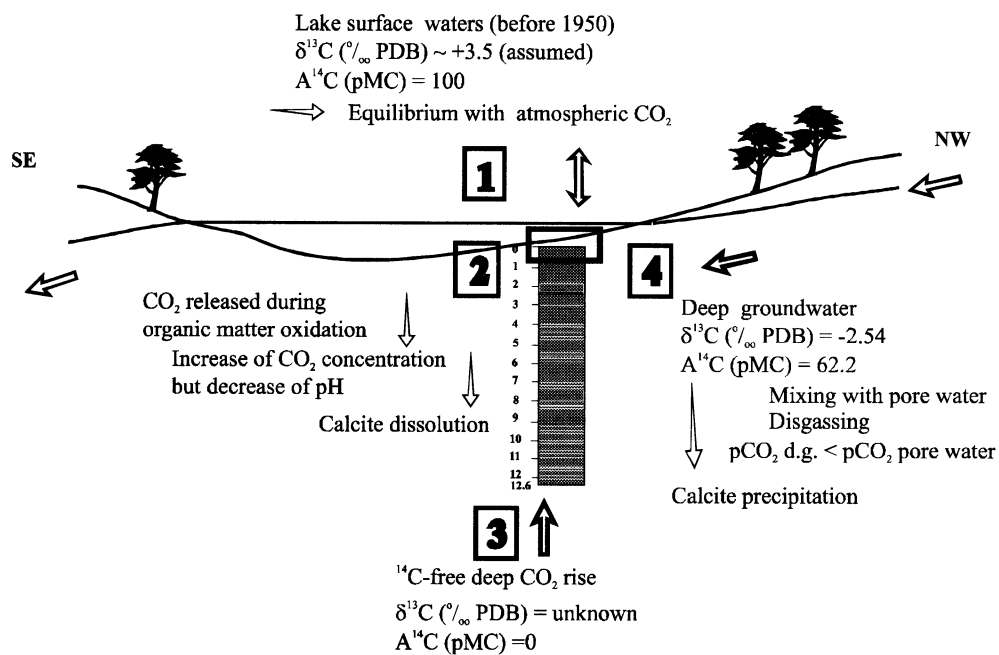


Figure 4 Processes of ^{14}C -free carbon incorporation in inorganic carbonates (Core ABII, 1995)

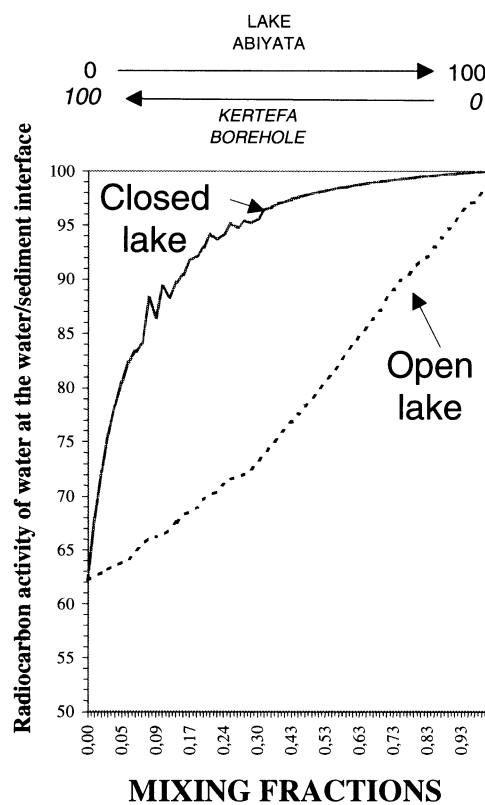


Figure 5 Mixing proportion between Lake Abiyata water and Kertefa groundwater at the water/sediment interface

Table 5 Mixing proportion between Lake Abiyata water and Kertefa groundwater at the water/sediment interface for every TOM/CaCO₃ ¹⁴C-dated level. See Figure 1 and Table 1 for sample locations and chemical characteristics, respectively.

Depth (cm)	Measured ¹⁴ C Age on TOM (yr BP)	Δ (yr BP)	Mixing part (%)			
			CLOSED LAKE		OPEN LAKE	
			POLE I (Lake)	POLE II (Groundwater)	POLE I (Lake)	POLE II (Groundwater)
7.0	100	480	17.7	82.3	81.5	18.5
551.8	3900	1500	6.6	93.4	59.0	41.0
671.5	4900	1500	7.1	92.9	60.1	39.9
794.8	5330	680	16.7	83.3	80.5	19.5
941.5	7900	800	14.1	85.9	77.0	23.0
984.5	8830	1000	11.1	88.9	71.8	28.2

□ Open Lake

○ Nearing closure

■ Closed Lake

CONCLUSION

Since organic matter is considered authigenic, the understanding of the carbon isotopic anomalies related to [CO₂(aq.)] as well as the relationships between and the CaCO₃-CO₂-organic matter system is crucial when comparing the isotopic signatures and discriminating or confirming the authigeny of the materials dated.

The ¹⁴C datings, as performed either on authigenic inorganic carbonates or on organic matter, show systematic discrepancies, ages obtained on carbonates always being older than those on organic matter. These differences are due to the geological and hydrogeological conditions and behavior of the study area. Although submitted to a very low hydraulic gradient, the presence of groundwater in the sedimentary basement of the lake brought us to consider the influence played on the crystallization and *geochemical* effects on the age of inorganic carbonates.

However, the observed discrepancy fits relatively well with the palaeohydrological phases already known on the basin (Street 1981; Gasse and Street 1978), and thus may help to validate paleoenvironmental reconstruction in the Lake Abiyata basin. The complete Holocene period is found within the first 12.6-m of core ABII. Despite a mean sedimentary rate of about 1.1 m/ka (Figure 3), which is in agreement with what is presently known about tropical lakes, the sedimentation rate is highly fluctuating: 1) 0.94 m ka⁻¹ before 10 ka BP; 2) 0.43 m ka⁻¹ between 10 and 4 ka BP; 3) 3.76 m ka⁻¹ between 4 and 3 ka BP; and 4) 1.42 m ka⁻¹ from 3 ka BP to present.

Since the ¹⁴C activity of lakebottom water reaches 111.8 pMC, it likely confirms that 1) the lake waters are well mixed, and 2) the mixing with groundwater takes place at the water-sediment interface. The precise, accurate study of chemical and isotopic contents of interstitial waters might allow for the validation of such paleoenvironmental reconstructions, and the modeling of the eventual diagenetical evolution during burial.

The important groundwater input, characterized by a specific isotopic signature quite different from the one of surface waters, can make very hazardous the paleoenvironmental reconstructions currently used and based on inorganic carbonates. In the present study, the comparison of the 2 chronologies, through the calculation of the respective proportions of ^{14}C and total carbon brought by each end-member in the mixing, allows for the quantitative estimation of this groundwater input.

In future perspectives, the study of interstitial waters would help to both 1) determine the stable isotope contents of pore waters, since they must be in agreement with those of groundwaters, and as a result; 2) solve the eventual problem of early diagenetical re-crystallization during burial.

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